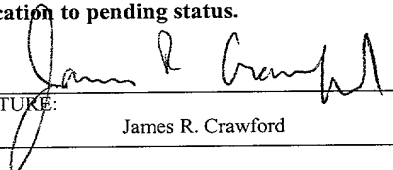


FORM PTO 1390 (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER <b>HUBR-1202</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <b>10/030033</b>
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/06952</b>	INTERNATIONAL FILING DATES <b>20 July 2000</b>	PRIORITY DATE CLAIMED <b>22 July 1999</b>	
TITLE OF INVENTION <b>POLYREACTIONS IN NON-AQUEOUS MINIEMULSIONS</b>			
APPLICANT(S) FOR DO/EO/US <b>Markus ANTONIETTI, Kathleen LANDFESTER, Mirjam WILLERT, Franca TIARKS, Nina BECHTHOLD</b>			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing 35 U.S.C. 371</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371 (f)). The submission must include items (5), (6), (9) and (21) indicated below.</li> <li>4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c)(2)) <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371 (c)(2)). <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto.</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input checked="" type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</li> <li>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> </ol>			
<b>Items 11 to 20 below concern document(s) or information included:</b>			
<ol style="list-style-type: none"> <li>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.</li> <li>14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</li> <li>15. <input type="checkbox"/> A substitute specification.</li> <li>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li>20. <input checked="" type="checkbox"/> Other items or information: PCT/IPEA/416</li> </ol>			

U.S. APPLICATION NO (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO		ATTORNEY'S DOCKET NUMBER	
10/030033		PCT/EP00/06952		HUBR-1202	
17. <input checked="" type="checkbox"/> The following fees are submitted:				<b>CALCULATIONS</b> PTO USE ONLY	
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b>					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....\$1040.00					
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .....\$890.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....\$740.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....\$710.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) .....\$100.00					
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$ 890.00	
Surcharge of \$ 130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$ 130.00	
<b>CLAIMS</b>	<b>NUMBER FILED</b>	<b>NUMBER EXTRA</b>	<b>RATE</b>		
Total claims	21 2 -20 =	1	X 18.00.	\$ 18.00	
Independent claims	1-3 =	0	X	\$	
MULTIPLE DEPENDENT CLAIM(s) (if applicable)				X	\$ 1038.00
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$ 1038.00	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$ 519.00	
<b>SUBTOTAL =</b>				\$ 519.00	
Processing fee of \$ _____ for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				\$	
<b>TOTAL NATIONAL FEE =</b>				\$ 519.00	
Fee for recording the enclosed assignment (37 CFR 1.21 (h)). Assignment Must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31) ( _____ per property).				+ \$	
<b>TOTAL FEES ENCLOSED =</b>				\$ 519.00	
				<b>Amount to be Refunded:</b>	\$
				<b>Charged:</b>	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>519.00</u> to cover the above fees is enclosed.					
b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required or credit any overpayment to my Deposit Account No. <u>50-0624</u> . A duplicate copy of this sheet is enclosed.					
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</b>					
SEND ALL CORRESPONDENCE TO: James R. Crawford FULBRIGHT & JAWORSKI L.L.P. 666 Fifth Avenue New York, New York 10103 (212) 318-3148 Customer No. 24972					
SIGNATURE: 				James R. Crawford	
NAME				39,155	



10/030033

531 Rec'd PCT/PTO 03 JAN 2002  
HUBR-1202 (10112687)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant(s) : Antonietti, et al.  
Based on : PCT/EP00/06952  
International Filing  
Date : July 20, 2000  
For : POLYREACTIONS IN NON-AQUEOUS MINIEMULSIONS

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January 3, 2002

Commissioner of Patents  
and Trademarks  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

S I R :

Prior to examination on the merits, please amend the above-identified patent application  
as follows:

**IN THE CLAIMS**

Cancel claims 1-21, without prejudice and substitute the following claims:

22. A method of conducting polymerizations in nonaqueous miniemulsions,  
comprising producing a miniemulsion from reactants of a polymerization in a  
nonaqueous fluid dispersing medium, using a surfactant and an osmotically  
stabilizing component, and is reacted.

23. The method as claimed in claim 22, wherein the polymerization is selected from addition polymerization reactions, polyaddition reactions, and polycondensation reactions.
24. The method as claimed in claim 23, wherein the polymerization comprises an addition polymerization of acrylic or styrene monomers.
25. The method as claimed in claim 23, wherein the polymerization comprises a polyaddition of polyfunctional epoxides with at least one of hydroxy, amino and thiol compounds.
26. The method as claimed in claim 23, wherein the polymerization comprises a polyaddition of polyfunctional isocyanates with at least one polyfunctional hydroxy or amino compounds.
27. The method as claimed in claim 23, wherein the polymerization comprises a polycondensation of polyfunctional carboxylic acids with polyfunctional hydroxy or amino compounds.
28. The method as claimed in claim 22, wherein a miniemulsion is formed from a disperse phase of polar reactants in a continuous apolar organic phase.
29. The method as claimed in claim 28, wherein hydrophilic substances, especially water or salts, are used as osmotically stabilizing component.
30. The method as claimed in claim 22, wherein a miniemulsion is formed from a disperse phase of apolar reactants in a continuous polar organic phase.

31. The method as claimed in claim 30, wherein hydrophobic substances are used as osmotically stabilizing component.
32. The method as claimed in claim 31, wherein the osmotically stabilizing component is added in an amount of from 0.1 to 40% by weight based on the overall weight of the emulsion.
33. The method as claimed in claim 32, wherein the average particle size of the emulsion is situated in the range from 30 to 600 nm.
34. The method as claimed in claim 33, wherein an emulsion is produced which is critically stabilized or thermodynamically stable with respect to an alteration in particle size.
35. The method as claimed in claim 34, wherein the emulsion further comprises dispersed therein particulate solids.
36. The method as claimed in claim 35, wherein the polymerization takes place without substantial alteration in the particle size.
37. The method as claimed in claim 22, wherein an inorganic polymerization is conducted in which a miniemulsion is produced from at least one of the reactants of an inorganic polymerization and is reacted.
38. The method as claimed in claim 22, wherein the inorganic polymerization comprises a preparation of metal salt particles, metal oxide particles or metal sulfide particles.

39. The method as claimed in claim 37, wherein a miniemulsion is formed from a disperse phase of an apolar reactant in a continuous polar organic phase.
40. The method as claimed in claim 37, wherein a miniemulsion is formed from a disperse phase of a polar reactant in a continuous apolar organic phase.
41. The method as claimed in 37, wherein the reaction takes place by addition of a further reactant of the inorganic polymerization by way of the continuous phase of the emulsion.
42. The method as claimed in claim 37, wherein the reaction takes place by addition of a further reactant of the inorganic polymerization by way of a further miniemulsion.

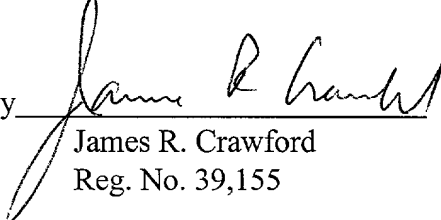
**REMARKS**

Early and favorable action on the merits is earnestly solicited.

It is not believed that any fees are due for entering this amendment. If it is determined that any fees are due, the Commissioner is authorized to charge such fees to Deposit Account No. 50-0624.

Respectfully submitted,

**FULBRIGHT & JAWORSKI L.L.P.**

By   
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characterized in that



**Polymerizations in nonaqueous miniemulsions****Description**

- 5 The invention relates to a method of conducting polymerizations in nonaqueous miniemulsions.

10 Miniemulsion polymerization is an innovative process of heterophase polymerization which extends the use of conventional emulsion polymerization. Miniemulsions are dispersions of two substantially immiscible phases and, if desired, one or more surfactants, in which unusually small droplet sizes are realized. In the case of polymerization reactions in miniemulsions, an apolar  
15 monomer or a mixture of monomers and, if desired, a cosurfactant are usually dispersed in water using a surfactant and high shear fields to form droplets of the desired order of magnitude, which are colloiddally stabilized by the added surfactant (Sudol and El-Aasser in: Emulsion Polymerization and Emulsion Polymers; Lovell, P.A.; El-Aasser, M.S., ed., Chichester (1997), 699). In such miniemulsions, the droplet size may grow  
20 further owing to collisions and fusions.

- 25 The German patent application 198 52 784.5-43 describes the osmotic stabilization of aqueous miniemulsions and microemulsions through the use of water-insoluble compounds as an emulsion-stabilizing component. By adding the water-insoluble substance to the oil phase,  
30 which is normally the disperse phase of the emulsion, an osmotic pressure is built up which counteracts the capillary pressure or Kelvin pressure built up with the surface tension of the emulsion droplets. This has the consequence of preventing or retarding Ostwald ripening  
35 of the emulsion droplets.

Nonaqueous dispersions are presently prepared primarily by inverse precipitation polymerization (Fengler and

Reichert, *Angew. Makromol. Chem.* 225 (1995), 139), inverse suspension polymerization (Lee and Hsu, *J. Appl. Polym. Sci.* 69 (1998) 229; Omidian et al., *Polymer* 40 (1999), 1753) or inverse microemulsion  
5 polymerization (Bicak and Sherrington, *Reactive Funct. Polym.* 27 (1995), 155; Candau et al. *J. Polym. Sci., Polym. Chem. Ed.* 23 (1985), 193; Graillat et al., *J. Polym. Sci., Polym. Chem.* 24 (1986), 427; Barton et al., *Angew. Makromol. Chem.* 237 (1996) 99, Barton and  
10 Stillhammerova, *Angew. Makromol. Chem.* 237 (1996), 113). In these cases, however, there is a change in particle size and particle number during the polymerization; in other words, mass transport via the water phase determines the kinetics and the composition  
15 of the polymers and polymer latices prepared.

Inorganic nanoparticles are likewise prepared by reaction in inverse microemulsions (Pileni, *Langmuir* 13 (1997), 2366; Pileni, *Supramol. Sci.* 5 (1998), 321,  
20 Pileni; *Cryst. Res. Techn.* 33 (1998), 1155; Adair et al., *Materials Sci. Eng. R* 23 (1998), 139; Delfort et al., *J. Colloid Interf. Sci.* 189 (1997), 151), although the formulatability of an inverse microemulsion places considerable restrictions with regard to synthesis  
25 concentration and amount and nature of the surfactant. Generally speaking, the mass flow density of such inorganic particle syntheses is very low and at the boundary of what is technically sensible.

30 Imhof and Pine (*J. Colloid Interf. Sci.* 192 (1997), 368) describe increasing the stability of nonaqueous emulsions by adding small amounts of a water-insoluble oil. The emulsions described therein, however, have an average particle size of more than 1  $\mu\text{m}$ , and so do not  
35 constitute microemulsions or miniemulsions.

Surprisingly it has been found that miniemulsions may also be formulated effectively in nonaqueous dispersion media, where they lead to well-defined and stable

polymer products in the form of latices. Here, for example, a polar monomer such as acrylic acid or hydroxyethyl metacrylate is introduced into an apolar solvent, e.g., a hydrocarbon such as hexadecane or cyclohexane, and is stabilized with a typical surfactant which for inverse systems has an HLB of preferably less than 7, such as Aerosol OT (sulfosuccinic acid bis-2-ethylhexyl ester sodium salt), Span<sup>®</sup>80 (sorbitan monooleate, Fluka) or KLE3729 (Goldschmidt), for instance. As an osmotically active reagent, moreover, use is made of a strong hydrophile such as water and/or a salt, examples being salts of the monomers such as sodium acrylate. In this way, osmotically stabilized microemulsions are obtained whose polymerization gives rise to inverse dispersions of polar polymers which can be used further directly but from which the polymer may also be isolated in a substantially water-free form. In comparison to the known inverse precipitation polymerization, the method of the invention has the advantage that the particle size of the dispersion is easier to adjust and that in the case of a copolymerization a more homogeneous polymer structure, and respectively a crosslinking density which can be adjusted easily and homogeneously, can be achieved. In comparison to inverse suspension polymerization, much smaller particles can be prepared.

Polar organic solvents such as formamide, dimethylacetamide or glycols may also be used as dispersion media for preparing miniemulsions in which hydrophobic substances, e.g., polymerizable monomers, may be dispersed. Here again, use is made of surfactants having an HLB, preferred for O/W systems, of more than 7, such as sodium dodecyl sulfate, for instance, and of an osmotic control reagent, in this case a hydrophobic substance. In this way, even water-sensitive monomers may be polymerized in dispersion, examples being methacryloyl chloride, ketimines, or monomers containing isocyanate and epoxide. The

resulting functional polymer products constitute important intermediates for the synthesis of further polymer products.

- 5 Inorganic polymerizations, as well, may be guided very advantageously in miniemulsions in organic nonaqueous media. Products obtained include inorganic polymers, glasslike nanoparticles or nanocrystals. Either an inverse or a reverse route may be chosen. In the case  
10 of the inverse synthesis route, aqueous solutions of inorganic - e.g., metallic - precursors are miniemulsified in hydrophobic organic solvents, the coreactant then being added by way of the continuous phase or admixed in the form of a second miniemulsion.  
15 In the case of the reverse synthesis route, a hydrophobic inorganic precursor, e.g., an organometallic compound, such as titanium tetraisobutoxide, is miniemulsified in a strongly polar organic solvent using a surfactant and an osmotic  
20 control substance, e.g., an ultrahydrophobic compound; any residual solubility of the precursor in the continuous phase is of minor significance. By adding a further coreactant, e.g., water, by way of the continuous phase, or in the form of a second  
25 miniemulsion, the polymerization is then initiated and leads to dispersed nanoparticles of controlled size and morphology.

- The end products obtained are inorganic nanoparticles,  
30 with a considerably higher space-time yield than in the prior art. Furthermore, it is also possible to obtain particles which could not be prepared hitherto owing to the lack of corresponding stable emulsion systems in the prior art.

35

The invention therefore firstly provides a method of conducting polymerizations in nonaqueous miniemulsions which is characterized in that an emulsion of reactants of a polymerization is produced in a nonaqueous fluid

dispersing medium, using a surfactant and an osmotically stabilizing component, and is reacted to give a dispersion of particles of the polymerization product in the medium.

5

Polymerizations in the sense of the present invention are reactions in which monomers or mixtures of monomers are reacted to polymers. One example of polymerizations are addition polymerizations, i.e., polymerizations  
10 which proceed steplessly without elimination of byproducts, examples being the preparation of acrylic and/or styrene polymers or copolymers of corresponding monomers or monomer mixtures.

15 Another example of polymerizations are polyaddition reactions, which proceed in stages without the elimination of byproducts, examples being the preparation of polyurethanes from polyfunctional hydroxy compounds and polyfunctional isocyanates, the  
20 preparation of polyureas from polyfunctional amines and polyfunctional isocyanates, and the preparation of polyepoxides from polyfunctional epoxides and polyfunctional amines, thiols and/or hydroxy compounds.

25 The polymerizations also include polycondensation reactions, which proceed in stages with elimination of byproducts, an example being unipolycondensations, which proceed with the participation of a single monomer, e.g., a hydroxycarboxylic acid or an amino  
30 acid, or in which two different monomers are involved, an example being the preparation of polyamides from polyfunctional carboxylic acids and polyfunctional amines or the preparation of polyesters from polyfunctional carboxylic acids and polyfunctional  
35 hydroxy compounds. Another example of polycondensation reactions are copolycondensations, in which more than two different monomers are involved. Other polymers too may be prepared by polycondensation from the corresponding monomers, e.g., polyimides, poly-

carbonates, amino resins, phenolic resins, polysulfides or urea resins.

The miniemulsion in which the polymerization is  
5 conducted may be prepared by using high shear yields,  
e.g., by means of a rod-type ultrasonicator, a jet  
disperser or a microfluidizer. The emulsion droplets  
are preferably situated within the order of magnitude  
10 of from 20 to 1000 nm, in particular from 30 to 600 nm  
average particle diameter. In one embodiment of the  
invention, a miniemulsion is formed from a disperse  
phase of polar organic monomers in a continuous apolar  
organic phase which is substantially miscible with the  
polar phase. In this embodiment, the osmotically  
15 stabilizing components used comprise hydrophilic  
substances, especially water and/or salts, including  
salts of the polar monomers, e.g., salts of acrylic  
acid or methacrylic acid.

20 In another embodiment, a O/W miniemulsion is formed  
from a disperse phase of apolar organic monomers in a  
continuous polar organic phase, the two phases being  
substantially immiscible. In this case, osmotically  
stabilizing components used comprise hydrophobic  
25 substances which mix with the apolar phase and have a  
solubility in the polar phase of preferably less than  $5 \times 10^{-5}$  g/l, with particular preference less than  $5 \times 10^{-6}$  g/l, and most preferably less than  $5 \times 10^{-7}$  g/l at  
room temperature. Examples thereof are hydrocarbons,  
30 especially volatile, optionally halogenated  
hydrocarbons, silanes, organosilanes, siloxanes, long-  
chain esters, oils such as vegetable oils, e.g., olive  
oil, hydrophobic dye molecules, blocked isocyanates,  
and also oligomeric addition polymerization,  
35 polycondensation, and polyaddition products.

The osmotically stabilizing components are added  
generally in an amount of from 0.1 to 40% by weight,  
preferably from 0.2 to 10% by weight, and with

particular preference from 0.5 to 5% by weight, based on the overall weight of the emulsion.

Also added for the purpose of stabilizing the O/W emulsion are surfactants such as sodium dodecyl sulfate, cetyltrimethylammonium chloride or else polymeric surfactants, such as block copolymers of styrene and ethylene oxide, for example. The amount of surfactant is preferably in the range from 0.1 to 20% by weight, more preferably from 0.2 to 10% by weight, with particular preference from 0.5 to 5% by weight, based on the overall weight of the emulsion.

The surfactants and osmotically stabilizing components are preferably selected so as to be compatible with the resultant polymerization product. Thus it is possible to use substances which possess a high volatility and/or which are usefully employed in the context of any further use of the polymeric dispersion, e.g., as plasticizers, dye, etc., so that they may contribute positively to the target application. By varying the surfactants and/or the osmotically stabilizing components and/or their amounts in the reaction batch it is possible to adjust as desired the particle size of the emulsion and of the resultant polymer dispersion.

The polymerization of the miniemulsion may also be initiated in a known way; for example, by adding a catalyst - a free-radical initiator, for example - and by raising the temperature. In this case, the preferred starting point is a critically stabilized emulsion, and with particular preference a thermodynamically stable emulsion. In the case of emulsions stabilized osmotically in this way, it is possible to obtain dispersions of the polymerization product whose particle sizes has not altered undesirably relative to that of the reactants emulsion. The particles of the polymerization product have an average size of

preferably from 10 to 1000 nm and with particular preference from 30 to 600 nm.

Furthermore, the method of the invention is also suitable for preparing multiphase nanohybrid particles, e.g., particles which comprise polymerization products and - encapsulated therein - inert particulate solids, e.g., inorganic materials such as metal colloids, oxidic particles such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{CaSO}_4$ ,  $\text{CaCO}_3$ ,  $\text{BaSO}_4$ , zeolites, iron oxides,  $\text{ZnO}$ ,  $\text{CoO}$ ,  $\text{CrO}_2$ ,  $\text{ZrO}_2$ , fluoroapatites and hydroxyapatites, and fine carbon black, or organic materials, such as colloidal dye aggregates. The size of the particulate solids is generally situated within the range from 0.5 to 400 nm, preferably in the range from 1 to 250 nm, and with particular preference in the range from 10 nm to 200 nm. The size of the emulsion droplets is tailored to the size of the particulate solids that are to be encapsulated.

With polymerization reactions in osmotically stabilized nonaqueous miniemulsions, it is possible to achieve efficient embedding of particulate solids into the shell of polymerization products. Preferably at least 60%, with particular preference at least 80%, more preferably still at least 90%, and most preferably at least 95% of the particulate solids are embedded. The dispersions obtained by polymerization may be filmed homogeneously, with the resultant films exhibiting high mechanical stability and acid resistance. Owing to the homogeneous encapsulation, the resultant nanohybrid particles may be used, for example, for paints or coatings with a high coloristic efficiency.

The invention further provides a method of conducting inorganic polymerizations in nonaqueous miniemulsions which is characterized in that a miniemulsion of at least one of the reactants of an inorganic polymerization is produced and is reacted.



An inorganic polymerization in the sense of the present invention is a polymerization in which at least one inorganic reactant is used and/or one inorganic reaction product is obtained. Examples of such inorganic polymerizations are the preparation of metal salt particles, metal oxide particles or metal sulfide particles.

10 In one embodiment of the method, a miniemulsion is formed from a disperse phase of an apolar reactant in a continuous polar organic phase, e.g., formamide, dimethylformamide, dimethylacetamide and/or dimethyl sulfoxide. The polymerization is then initiated by adding one or more further reactants by way of the continuous phase and/or in the form of a second miniemulsion. One example of this embodiment is the preparation of metal oxide particles from organometallic precursor compounds and water, in which water can be added by way of the continuous phase.

In another embodiment of the invention, an aqueous or nonaqueous miniemulsion is formed from a disperse phase of a polar reactant in a continuous apolar organic phase which is substantially immiscible with the disperse phase. Here again, the polymerization may be initiated by adding one or more further reactants by way of the continuous phase and/or in the form of a second miniemulsion. An example of this embodiment is the preparation of metal sulfide particles in which a miniemulsion of an aqueous solution of polar precursors, e.g., metal salts, in an apolar organic phase is produced, then a second miniemulsion containing sulfide ions is added, and these miniemulsions are mixed by applying corresponding shear fields and stimulated to undergo droplet exchange.

In the conduct of inorganic polymerizations, it is preferred to add surfactants and/or osmotically

stabilizing components (in the amounts indicated before) in order to stabilize the miniemulsions. The other preferred features in the context of the above-described organic polymerizations, as well, are transferable to the conduct of inorganic polymerizations.

Furthermore, the invention is to be illustrated by means of the following figures and examples:

10

Figure 1 shows an electron micrograph of PbS particles prepared by the method of the invention,

15

Figures 2 and 3 show electron micrographs of BaSO<sub>4</sub> particles prepared by the method of the invention, immediately following their formation (Fig. 2) and after 6-day maturation (Fig. 3).

20

#### **Example**

#### **Example 1**

25 1 g of acrylic acid was admixed with 60 mg of water and added to a solution of 9 g of cyclohexane and 250 mg of the surfactant KLE3729 (Goldschmidt AG). After the mixture had been stirred for 1 h at the highest magnetic stirrer setting, it was miniemulsified using a  
30 rod-type ultrasonicator (Branson Sonifier, W400 Digital, Amplitude of 70%) for 60 s. The miniemulsion was heated to 65°C and the polymerization was initiated with 50 mg of azobisisobutyronitrile (AIBN). After 12 h, complete conversion was reached.

35

The particle size was measured using a Nicomp Particle Sizer (Model 370, PSS, Santa Barbara, USA) at a fixed scatter angle of 90°. The molecular weights of the polymers were determined by means of GPC analysis,

carried out using a P1000 pump and a UV1000 detector (Thermo Separation Products) at a wavelength of 260 nm with 5  $\mu$ m 8x300 mm SDV columns with  $10^6$ ,  $10^5$ , and  $10^3$  angströms respectively (Polymer Standard Service) in  
5 THF with a flow rate of 1 ml/min at 30°C. The molecular weights were calculated on the basis of a calibration relative to the standards.

Electron micrographs were taken using a Zeiss 912 Omega  
10 electron microscope at 100 kV. The diluted particle dispersions were applied to a 400 mesh carbon coated copper grid and left to dry.

The average particle size of the resulting dispersion  
15 was approximately 50 nm.

#### **Example 2**

In accordance with the instructions of example 1,  
20 acrylic acid to which diethylene glycol diacrylate (DEGDA) had been added (degree of crosslinking 1:40) was polymerized. Here again, stable particles in the form of hydrogels were obtained.

25 The result of this experiment is shown in table 1.

#### **Example 3**

Instead of cyclohexane, hexadecane was used as the  
30 dispersion medium. In accordance with the instructions described in example 1, dispersions were prepared.

The result of this experiment is shown in table 1.

#### **Example 4**

The amount of surfactant in example 3 was varied. It was possible to formulate stable inverse miniemulsions in the range from 2 to 100 w% surfactant, preferably

from 10 to 50 w% surfactant. The indication of the amount of surfactant in "w%" refers to the weight of the monomer and, respectively, of the resulting polymer.

5

The results are shown in table 1.

#### Example 5

10 Instead of KLE3927, the surfactants Span 80, C<sub>18</sub>E<sub>10</sub>, and AOT were used. Here too, it was possible to obtain polymer dispersions.

#### Example 6

15

Instead of acrylic acid, other hydrophilic monomers such as hydroxymethyl methacrylate (HEMA), acrylamide, and isopropylacrylamide, for instance, were polymerized.

20

a) 3 g of hydroxymethyl methacrylate were admixed with 125 mg of water, added to a solution of 25 g of cyclohexane and 300 mg of the surfactant KLE3729, and stirred for 1 h at the highest magnetic stirrer setting. In accordance with the instructions described in example 1, a miniemulsion was prepared and reacted. The particle size of the resulting polymer dispersion was approximately 130 nm (see table 2).

30

b) 3 g of acrylamide or isopropylacrylamide were admixed with 4 mg of water, added to a solution of 32 g of cyclohexane or hexane, respectively, and 500 mg of the surfactant KLE3729, and stirred for 1 h at the highest magnetic stirrer setting. In accordance with the instructions described in example 1, a miniemulsion was prepared and reacted. The particle size of the resulting dispersion was approximately 90 nm (see table 2).

35

It was also possible to produce dispersions following variation of the dispersing media, surfactants, surfactant amounts, and the initiator (see table 2).

5

#### **Example 7**

6 g of styrene and 250 mg of hexadecane (HD) were added to a solution of 24 ml of formamide and 72 mg of sodium dodecyl sulfate and mixed for 1 h with the magnetic stirrer setting on full. Using a rod-type ultrasonicator (1 min, amplitude of 90%), a miniemulsion was prepared. The polymerization was conducted at 72°C using 120 mg of  $K_2S_2O_8$  (KPS) as initiator. After 6 h, the reaction was at an end. Highly stable polymer dispersions in the formamide organic medium were obtained.

When the amount of surfactant was increased to up to 500 mg it was found that the particle size can be adjusted by way of the amount of surfactant.

When using the nonionic surfactant Lutensol AT50 (amounts 125-1000 mg), it was also possible to produce stable polymer dispersions having particle sizes of between 70 and 250 nm.

The results are shown in table 3.

#### **Example 8**

Instead of formamide, glycol is used as the dispersion medium. Otherwise, the procedure described in example 7 was followed. Stable dispersions were obtained which had a much larger particle size than the corresponding formamide dispersions.

The results are shown in table 4.

### Example 9

Hydrolysis-sensitive monomer substances such as glycy methacrylate, for example, were polymerized in accordance with the instructions described in example 7.

### Example 10

In accordance with the instructions described in example 7, a polymer dispersion was prepared in dimethylacetamide (DMA).

### Example 11

1 g of titanium(IV) isopropoxide was added to a solution of 10 ml of formamide and 130 mg of Lutensol AT50 and mixed for 1 h with the magnetic stirrer setting on full. Using a rod-type ultrasonicator (1 min, amplitude of 90%), a miniemulsion was prepared. By careful addition of a 10% strength aqueous formamide solution, stable  $\text{TiO}_2$  dispersions were prepared.

### Example 12

Two miniemulsions were formulated, with one miniemulsion containing droplets with heavy metal salts, e.g., Pb, Zn or Cd salts, in the form of acetates, for example, and the other miniemulsion containing droplets with  $\text{Na}_2\text{S}$ . After mixing, the systems were subjected to shearing, and stable metal sulfide dispersions were obtained.

#### 1. Preparation of a PbS dispersion

*1<sup>st</sup> miniemulsion:* 270 mg of  $\text{PbNO}_3$  were dissolved in 1 ml of water (final concentration 1 M). The salt solution was added to a mixture of 125 mg of surfactant (KLE3729 or Span®80) and 10 g of cyclohexane and stirred for an

hour at the highest magnetic stirrer setting. Miniemulsification was carried out using a rod-type ultrasonicator (Branson Sonifier, W400 Digital, amplitude of 70%) for 60 s.

5

*2nd miniemulsion:* 238 mg of  $\text{Na}_2\text{S}$  were dissolved in 1 ml of water (final concentration 2 M). The salt solution was added to a mixture of 125 mg of surfactant (KLE3729 or Span®80) and 10 g of cyclohexane and stirred for an hour at the highest magnetic stirrer setting. Miniemulsification was carried out using a rod-type ultrasonicator (Branson Sonifier, W400 Digital, amplitude of 70%) for 60 s.

10

The two miniemulsions were combined and treated with ultrasound for 60 s. The particle size was approximately 130 nm when using KLE3729 and approximately 50 nm when using Span 80. Fig. 1 shows the PbS particles when using KLE3729.

20

## **2. Preparation of a $\text{BaSO}_4$ dispersion**

*1<sup>st</sup> miniemulsion:* 37.5 mg of  $\text{BaCl}_2$  were dissolved in 1.5 ml of water (final concentration 0.1 M). The salt solution was added to a mixture of 250 mg of surfactant (Aerosol OT or Span®80) and 6 g of cyclohexane and stirred for an hour at the highest magnetic stirrer setting. Miniemulsification was carried out using a rod-type ultrasonicator (Branson Sonifier, W400 Digital, amplitude of 70%) for 60 s.

25

30

*2nd miniemulsion:* 21 mg of  $\text{Na}_2\text{SO}_4$  were dissolved in 1.5 ml of water (final concentration 0.1 M). The salt solution was added to a mixture of 250 mg of surfactant (Aerosol OT or Span®80) and 6 g of cyclohexane and stirred for an hour at the highest magnetic stirrer setting. Miniemulsification was carried out using a rod-type ultrasonicator (Branson Sonifier, W400 Digital, amplitude of 70%) for 60 s.

35

The two miniemulsions were combined and treated with ultrasound for 60 s. The particle size was approximately 15 nm directly following ultrasound treatment and approximately 30 nm after 6-day maturation. Fig. 2 shows particles directly after the ultrasound treatment, fig. 3 after 6-day maturation.



Table 1:

Monomer		Continuous phase		Emulsifier		Hydrophobe/ hydrophile		Initiator		Particle size (nm)
Acrylic acid	1 g	HD*	9 g	KLE3729	500 mg	H <sub>2</sub> O	60 mg	AIBN	40 mg	58
Acrylic acid + DEGDA*	1 g	HD	9 g	KLE3729	500 mg	H <sub>2</sub> O	58 mg	AIBN	51 mg	53
Acrylic acid + DEGDA	1 g	HD	9 g	KLE3729	254 mg	H <sub>2</sub> O	78 mg	AIBN	52 mg	50
Acrylic acid + DEGDA	1 g	HD	10 g	KLE3729	127 mg	H <sub>2</sub> O	85 mg	AIBN	50 mg	78
Acrylic acid + DEGDA	1 g	CH*	11 g	KLE3729	126 mg	H <sub>2</sub> O	72 mg	AIBN	50 mg	78
Acrylic acid + DEGDA	1 g	CH	9 g	KLE3729	253 mg	H <sub>2</sub> O	76 mg	AIBN	50 mg	50

\*HD: Hexadecane; CH: cyclohexane, DEGDA: diethylene glycol diacrylate (molar ratio 1:80)

Table 2

Monomer	Continuous phase		Emulsifier		Hydrophobe/hydrophile		Initiator		Particle size (nm)
Acrylamide in H <sub>2</sub> O	3 g	Hexane	Span80	513 mg			AIBN in hexane	80 mg	85/265
	4 g							5 ml	
Acrylamide in H <sub>2</sub> O	3 g	CH	KLE3729	500 mg			AIBN in CH	100 mg	91
	4 g								
Acrylamide in H <sub>2</sub> O	3 g	CH	KLE3729	250 mg			AIBN in CH	100 mg	101
	4 g								
Acrylamide in H <sub>2</sub> O	3 g	CH	KLE3729	125 mg			AIBN in CH		138
	4 g								
Isopropyl-acrylamide in H <sub>2</sub> O	1.5g	CH	KLE3729	500 mg			AIBN in CH		91
	7.5g								
HEMA	3 g	CH	KLE3729	300 mg	H <sub>2</sub> O	125 mg	PEGA200	64 mg	129
HEMA	3 g	CH	KLE3729	500 mg	H <sub>2</sub> O	125 mg	PEGA200	100 mg	102
HEMA	3 g	CH	KLE3729	500 mg	H <sub>2</sub> O	125 mg	AIBN	60 mg	78
HEMA	2 g	HD	KLE3729	510 mg	H <sub>2</sub> O	60 mg	PEGA200	108	84

CH: Cyclohexane, HD: Hexadecane; HEMA: Hydroxyethyl methacrylate

Table 3

Monomer		Continuous phase		Emulsifier		Hydrophobe/ hydrophile		Initiator		Particle size (nm)
Styrene	6 g	Formamide	24 ml	SDS	125 mg	HD*	250 mg	KPS*	120 mg	251
Styrene	6 g	Formamide	24 ml	Lutensol AT50	507 mg	HD*	266 mg	KPS	120 mg	71
Styrene	6 g	Formamide	24 ml	SDS	74 mg	HD	250 mg	KPS	120 mg	220
Styrene	6 g	Formamide	24 ml	SDS	252 mg	HD	270 mg	KPS	121 mg	183
Styrene	6 g	Formamide	24 ml	SDS	502 mg	HD	252 mg	KPS	121 mg	188
Styrene	6 g	Formamide	24 ml	Lutensol AT50	126 mg	HD	279 mg	KPS	120.5 mg	253
Styrene	6 g	Formamide	24 ml	Lutensol AT50	252 mg	HD	280 mg	KPS	120 mg	138

\*HD: hexadecane; KPS:  $K_2S_2O_8$

- 20 -

Table 4

Monomer		Continuous phase		Emulsifier		Hydrophobe/ hydrophile		Initiator		Particle size* (nm)
Styrene	6 g	glycol	27.6g	Lutensol AT50	503 mg	HD**	264 mg	KPS**	120 mg	386
Styrene	6 g	glycol	40 g	SDS	50 mg	HD	259 mg	KPS	122 mg	***
Styrene	6 g	glycol	40 g	SE3030	2 g	HD	261 mg	KPS	120 mg	144
Styrene	6 g	glycol	24 g	PEO/PPO	1 g	HD	250 mg	KPS in glycol	122 mg	104

\* diluted with water

5 \*\* HD: hexadecane; KPS:  $K_2S_2O_8$

\*\*\* not measured

**Claims**

1. A method of conducting polymerizations in nonaqueous miniemulsions,  
5 **characterized in that**  
a miniemulsion is produced from reactants of a polymerization in a nonaqueous fluid dispersing medium, using a surfactant and an osmotically stabilizing component, and is reacted.
- 10 2. The method as claimed in claim 1,  
**characterized in that**  
the polymerization is selected from addition polymerization reactions, polyaddition reactions,  
15 and polycondensation reactions.
3. The method as claimed in claim 2,  
**characterized in that**  
the polymerizations comprises an addition  
20 polymerization of acrylic and/or styrene monomers.
4. The method as claimed in claim 2,  
**characterized in that**  
the polymerization comprises a polyaddition of  
25 polyfunctional epoxides with hydroxy, amino and/or thiol compounds.
5. The method as claimed in claim 2,  
**characterized in that**  
30 the polymerization comprises a polyaddition of polyfunctional isocyanates with polyfunctional hydroxy and/or amino compounds.
6. The method as claimed in claim 2,  
35 **characterized in that**  
the polymerization comprises a polycondensation of polyfunctional carboxylic acids with polyfunctional hydroxy and/or amino compounds.

7. The method as claimed in any of claims 1 to 6,  
**characterized in that**  
a miniemulsion is formed from a disperse phase of  
5 polar reactants in a continuous apolar organic  
phase.
8. The method as claimed in claim 7,  
**characterized in that**  
10 hydrophilic substances, especially water and/or  
salts, are used as osmotically stabilizing  
component.
9. The method as claimed in any of claims 1 to 6,  
**characterized in that**  
15 a miniemulsion is formed from a disperse phase of  
apolar reactants in a continuous polar organic  
phase.
- 20 10. The method as claimed in claim 9,  
**characterized in that**  
hydrophobic substances are used as osmotically  
stabilizing component.
- 25 11. The method as claimed in any of the preceding  
claims,  
**characterized in that**  
the osmotically stabilizing component is added in  
an amount of from 0.1 to 40% by weight based on  
30 the overall weight of the emulsion.
12. The method as claimed in any of the preceding  
claims,  
**characterized in that**  
35 the average particle size of the emulsion is  
situated in the range from 30 to 600 nm.
13. The method as claimed in any of the preceding  
claims,

**characterized in that**

an emulsion is produced which is critically stabilized or thermodynamically stable with respect to an alteration in particle size.

5

14. The method as claimed in any of the preceding claims,

**characterized in that**

the emulsion further comprises - dispersed therein - particulate solids.

10

15. The method as claimed in any of the preceding claims,

**characterized in that**

the polymerization takes place without substantial alteration in the particle size.

15

16. A method of conducting inorganic polymerizations in nonaqueous miniemulsions,

**characterized in that**

a miniemulsion of at least one of the reactants of an inorganic polymerization is produced and reacted.

20

25 17. The method as claimed in claim 16,

**characterized in that**

the inorganic polymerization comprises a preparation of metal salt particles, metal oxide particles or metal sulfide particles.

30

18. The method as claimed in claim 16 or 17,

**characterized in that**

a miniemulsion is formed from a disperse phase of an apolar reactant in a continuous polar organic phase.

35

19. The method as claimed in claim 16 or 17,

**characterized in that**

a miniemulsion is formed from a disperse phase of a polar reactant in a continuous apolar organic phase.

- 5    20.    The method as claimed in any of claims 16 to 19,  
         **characterized in that**  
         the reaction takes place by addition of a further  
         reactant of the inorganic polymerization by way of  
         the continuous phase of the emulsion.

10

21.    The method as claimed in any of claims 16 to 19,  
         **characterized in that**  
         the reaction takes place by addition of a further  
         reactant of the inorganic polymerization by way of  
15       a further miniemulsion.





11

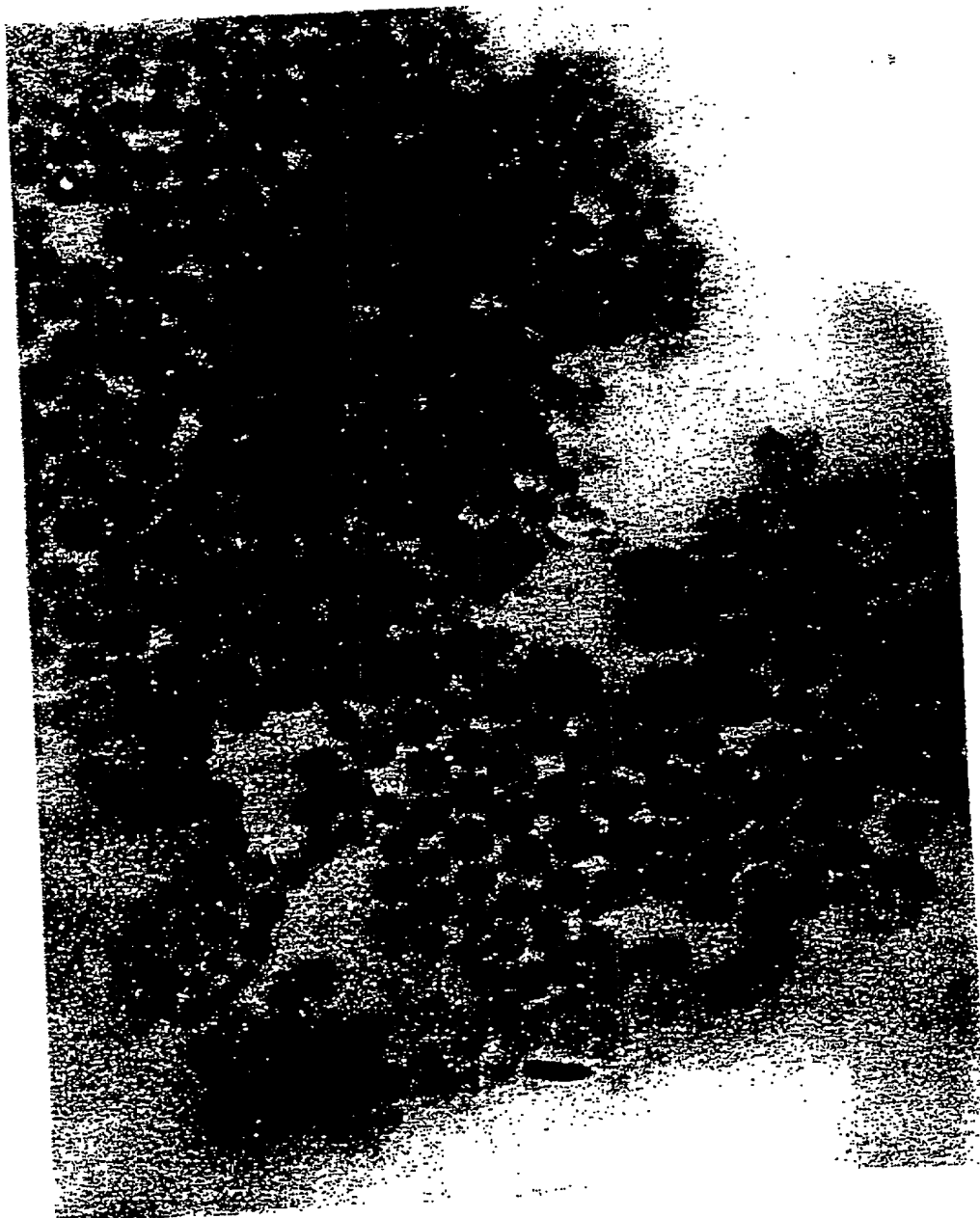


Fig. 1



Fig. 2

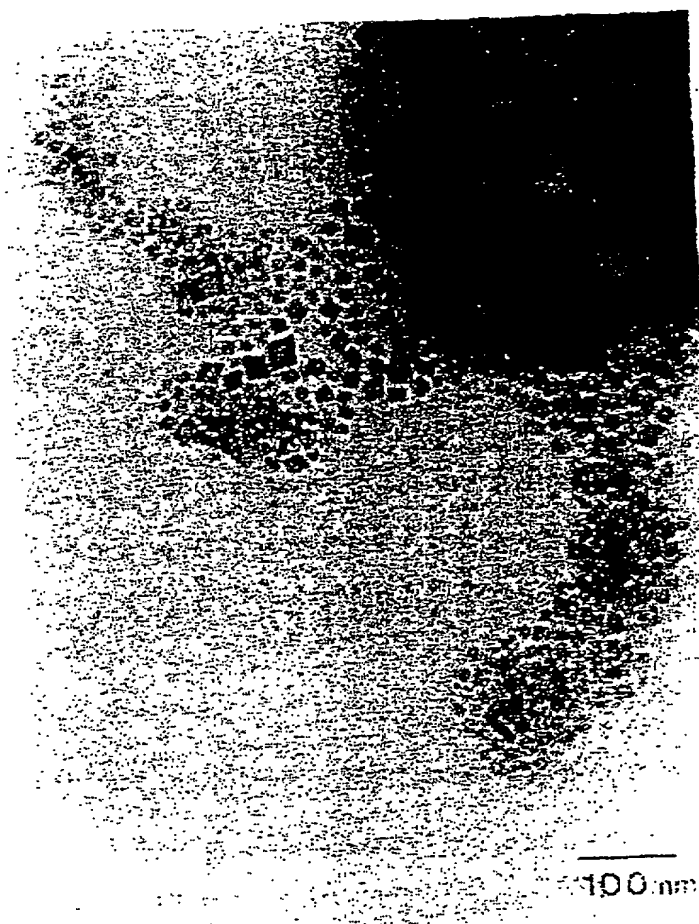



Fig. 3

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PTO/SB/01 (4-96)

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Attorney Docket Number HUBR 1202

First Named Inventor Antonietti

## COMPLETE IF KNOWN

Application Number 10/030,033

Filing Date January 3, 2002

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

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Polymerizations in nonaqueous miniemulsions

(Title of the invention)

the specification of which

☐ is attached hereto

OR

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as United States Application Number or PCT International

Application Number PCT/EP00/06952 and was amended on (MM/DD/YYYY) Aug 27, 2001 (if applicable).

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Given Name (first and middle (if any))	Family Name or Surname
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ADDITIONAL INVENTOR(S)  
Supplemental Sheet

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Inventor's Signature	Mirjam Willert				Date	10.1.2002	
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Given Name	Franca	Middle Initial		Family Name	Tiarks	Suffix e.g. Jr.	
Inventor's Signature	Franca Tiarks				Date	6.1.2002	
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Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
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Inventor's Signature	Nina Bechthold				Date	9.1.2002	
Residence: City	Potsdam Essen	State		Country	Germany	Citizenship	DE
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